THE EFFECT OF CARRIER GAS ON THE ENTRAINED BED PYROLYSIS OF WESTERN KENTUCKY No. 9 COAL.

by

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INTRODUCTION

Flash pyrolysis in different gases has been studied as an alternative process for the simultaneous gasification and liquefaction of coal. Experimental studies on flash hydropyrolysis, steam pyrolysis, and inert gas pyrolysis of various types of coal have been reported in the literature (1-26). Investigations on the effect of steam and hydrogen on the pyrolysis of hydrocarbons, coal and vacuum residue (24, 27) indicate that both steam and hydrogen influence the yield. Szuba and Michalik (24) have shown that the total production of liquids from pyrolysis is higher in the presence of steam than in an inert atmosphere, but is still lower than the liquid production from hydropyrolysis. These studies have examined in detail, the effect of the process variables (temperature, pressure, solids contact time, gas phase residence time, etc.) on the total yield of products and on the selectivity of the reaction.

However, there is a lack of liquid product characterization. Simple analytical techniques such as gas chromatography and elemental analysis do not provide enough information on their nature. This is due to the chemical complexity of these liquids and the large number of individual components.

Adequate characterization of the liquid obtained is important in the evaluation of a coal liquefaction process. In the industrial operation of upgrading coal liquids, three factors must be considered. The first is the known instability of these liquids upon heating in the presence of oxygen, i.e. their tendency to polymerize. The second is that that the removal of heteroatoms calls for expensive upgrading in a catalytic reaction that consumes hydrogen heavily. The last consideration is that the liquid has to be reformed to a desired molecular size and carbon to hydrogen ratio. The liquefaction products need characterization to provide information on which and how much of this processing is required.

Hydrocarbon liquid production by coal pyrolysis in an inert gas is not attractive as an industrial process. It yields low conversions, produces unstable liquids, and has low selectivity towards desirable products. As a result, more emphasis is placed on hydropyrolysis and steam pyrolysis. These two processes involve different chemical reactions. Present interest in flash steam pyrolysis stems from the economical advantage of using steam in place of expensive hydrogen, and from that steam has higher selectivity than inert gas towards the production of desirable liquids (10). A knowledge of the differences between hydrogen and steam pyrolysis

products and reaction mechanisms is useful when considering both
processes as potential routes to liquid and gaseous fuels. The goal
of this research project was to find a meaningful way of
characterizing the products and to apply this characterization to
steam and hydrogen pyrolysis liquids.

To achieve these objectives, coal was treated under identical
reaction pressure and temperature in three reaction environments:
hydrogen, a steam/helium mixture, and pure helium. A comparison was
then made on the effect of the reaction environment on the gas and
liquid yields. The characterization technique was used then, to
establish the structure of the major fractions of components in the
liquids produced by hydrogen and steam/helium pyrolysis. The
analogies and differences between different parts of the liquids,
their dependence upon the reaction environment and the chemical
reactions that explains the differences which are discussed in this
paper.

THE CHARACTERIZATION TECHNIQUE

Previous experience with the characterization of pyrolysis
derived liquids in our laboratory has shown the limitations of
conventional analytical techniques (10). For example, the
gas-chromatographic separation of the liquids failed to elute a
significant part of the liquid. Most of the material remained in the
column.

The characterization of groups in coal derived liquids has been
used widely. The information obtained by hydrogen and carbon NMR and
FTIR has been very useful in elucidating the functional structure of
the liquid. Functional characterization of the liquid, however, is
not enough to characterize the physical and chemical properties of the
liquid. It is also necessary to establish to what kind of molecule
the functional group is attached, its molecular size and other groups
in the molecule. Also, it is essential to know how functional groups,
molecular sizes and other properties (such as aromaticity) are
distributed in the liquid.

With a simple liquid mixture, the obvious answer would be to
separate all components and identify them. With coal pyrolysis
liquids, with hundreds of individual components, this is not a
practical solution. Even if such a laborious task is accomplished, the
components should be lumped in families with some common properties,
to make any practical use of the results of the separation.

Sequential Elution Solvent Chromatography (SESC) (28, 29) is a
technique that was developed for the separation of coal liquefaction
products in several fractions. Each fraction has some common
features, such as characteristic functional groups, polarity or
basicity. SESC offered for our application a balance point between
detail in the separation and low number of fractions separated.
Although SESC was not applied to the characterization of coal
pyrolysis liquids before this work, the theory of the method was
applicable to coal pyrolysis products and the probabilities of
success were high.

In preliminary work with the technique, we found that no fraction
did elute with pyridine as a solvent. We did eliminate pyridine from
the sequence. Since the method is not the original SESC of Farcasiu
(28), it will be called modified-SESC or M-SESC in this paper.

Following the separation, each fraction was further characterized by Steric Exclusion HPLC (molecular size distribution), Boiling Point Distribution (GC method), H-NMR (aromatic and aliphatic H, H containing functional groups), Elemental Analysis and density.

The information obtained is useful as a more detailed and accurate model of the coal liquid obtained by pyrolysis. The information can be used to discuss the characteristics of the reaction paths during pyrolysis in different gas environments, as shown in this paper.

EXPERIMENTAL

The coal used was Western Kentucky No. 9 (from the Pyro Mine, Kentucky). The composition of the coal is given in Table I.

The pyrolysis system was operated in 6.9 MPA with pure hydrogen, pure helium, or a mixture of 7.6 mole percent of steam in helium. Coal was fed at a rate of 1 kg/hr into the reactor which was 7.9 cm in diameter and 100 cm in length. All the tests were conducted at 740 C in a 30 cm long hot zone. The superficial velocity of the gases fed into the reactor varied from 5 to 8 cm/s. For the hydrogen and steam/helium runs, the free falling coal particles were maintained in the hot reactor zone for one second. Full details of this apparatus are given elsewhere(4).

The liquids from the steam/helium and hydrogen runs were then characterized. Note that the helium run was included solely to assess the effect of reaction environment on the total yield and thus was not further analyzed. An account of the experimental details of the M-SESC fractionation and the characterization of each fraction has been given by Shen (32).

RESULTS

A comparison of the products from coal pyrolysis in hydrogen, the steam/ helium mixture, and pure helium is presented in Figure 1. The overall yield from steam pyrolysis is higher than the yield from inert gas (helium) pyrolysis under the same operating conditions. The data for the three processes reveal that hydropyrolysis produces the largest amount of coal-derived products. The liquid products from the hydrogen and the steam/helium runs were further analyzed and the results are presented below.

Table II gives the elemental composition of the liquid products. Figure 2 shows the results of the Modified SESC (M-SESC) fractionation of the coal liquids. Figures 4 and 5 give the results of the elemental analyses of the Modified SESC fractions from both of the coal-derived liquids.

The boiling point distribution analysis of the M-SESC fractions for both liquids shows a boiling range of 50 to 400 C for Fraction I, and of 300 to 550 C for Fractions II and III. Fractions IV and higher did not elute from the GC column.

From the experimental molecular size distribution curves, the number average molecular weights were calculated with the formulas given by Schanne and Haemel (30). The average molecular weights of the M-SESC fractions are given in Figure 3.

Figures 6 and 7 summarize the information obtained from H⁼NMR spectroscopy of the samples and fractions analyzed. The proton spectra are used primarily for the determination of the percentages of aromatic and aliphatic hydrogen contained in each sample.

DISCUSSION

The structure of the M⁼SESC fractions, as obtained in the present research, is summarized in table 3. The table reports the common features of each fraction for both liquids. Behind the similarities between corresponding fractions, however, there are also significant differences between the two coal liquids. These differences reflects chemical reactions that occur under the influence of different gas environments.

Figure 8 shows a list of the chemical reactions that can play a role in coal pyrolysis in hydrogen, steam and inert gas. The differences between the properties of the liquids obtained in different gases can be attributed to these chemical reactions. In the following discussion, an attempt is made to explain our experimental results with the reactions of figure 8.

Analysis of Results

Figure 1

Steam Pyrolysis produces higher COx yields than the other pyrolysis processes, due to reaction (15) (carbon steam gasification). In He and H2, COx is probably produced from the decomposition of carboxylic and carbonyl groups. The production of light hydrocarbon gases is enhanced in H2 due to reactions (4) (capping of alkyl radicals), (8) (thermal dealkylation) and (11) (thermal hydrogasification). Pyrolysis in He or Steam can yield light hydrocarbon gases only from (1) (cracking) and (4) (hydrogen abstraction from another molecule). The yield of BTX is enhanced in the presence of hydrogen through reactions (5) and (7) (capping of single ring aromatic radicals), (9) (thermal hydrocracking of several⁼ring molecules),(8) (thermal dealkylation of alkyl⁼benzenes) and reactions (12), (13) and (14) (side chain heteroatom removal). The yield of liquids (heavier than BTX) in hydrogen is higher than in inert gas through reactions (5) and (7) (several⁼ring aromatic free radical capping) which competes with reaction (6) (recombination to form char). However, the yield is less than in steam, since hydrogen participates in reactions that break down large molecules, such as (8) (thermal dealkylation) (9) (thermal hydrocracking) and (10) (thermal hydrogenation, facilitates hydrocracking). In steam, the yield of liquids is higher than in inert gas. A tentative explanation is that reaction (15) may open the coal matrix, liberating fragments. Another possibility is the participation of steam in the breakdown of the virgin coal (reactions (1), (2) and (3)), through a heterolytic mechanism. The total conversion of coal by pyrolysis in hydrogen gives the highest yield, through reactions (5) and (7) which compete with reaction (6) (recombination to form char). The total conversion in steam pyrolysis is higher than in He due to reaction (15) (char gasification) and to an enhancement of the liquid yield, previously discussed.

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Figure 2

Fractions 1 and 2 in hydrogen pyrolysis are increased from fractions 3, 4 and 5 through reactions (9) (thermal hydrocracking) and (12), (13) and (14) (heteroatoms removal). Fraction 6 in hydrogen pyrolysis (very basic heteroatoms) could be increased from coal through reactions (5) and (7) or from fraction 5 through the elimination of acid groups, reaction (14). The fraction is not converted easily, since the basic heterocyclics have to be first hydrogenated through reaction (10) and the ring opened by hydrogenolysis (reaction similar to (9)) before reactions (12), (13) and (14) could proceed. Fraction 9 in both liquids (material not eluted from the M-SESC column) is probably a degradation product (coke), insoluble.

Figure 3

Fractions 1, 2, 3, 4, 5 and 6 of the hydrogen pyrolysis liquids have higher molecular weight than the corresponding steam pyrolysis liquids. Smaller molecules in these fractions can be converted to BTX and gas through reactions (9) (thermal hydrocracking) and (11) (thermal hydrogasification). The larger molecules in these fractions may be more difficult to break, hence increasing the average molecular weight of the fraction.

Figure 4

The nitrogen content of the hydrogen pyrolysis liquids fractions 1 and 2 is virtually zero, lower than in the steam pyrolysis liquids. This is due to its elimination from the fractions by hydrogen through reaction (13). In other fractions, nitrogen appears in the heterocyclic form, basic, and is more difficult to eliminate, as discussed before. The hydrogen content is comparable in the fractions of both liquids, although higher in hydrogen pyrolysis fraction 1, the most abundant. There is an upward trend in both liquids: higher fractions contain more hydrogen.

Figure 5

The carbon content in the fractions of both liquids is comparable. The downwards trend is required to accommodate the higher heteroatoms content of the higher fractions. Oxygen + sulphur in both liquids follow an upwards trend, in agreement with the SESC fractionation theory. Fractions 1 and 2, the most abundant, show less heteroatoms in hydrogen pyrolysis, confirming the influence of reactions (12) and (14). Other fractions (heterocyclics) do not show the same effect, due to the difficulty associated with breaking ring heteroatoms.

Figure 6

The fractions in both liquids follow an upwards trend, higher fractions have a higher hydrogen to carbon ratio. There are differences between the two liquids, but they do not follow a clear trend.

Figure 7

Fractions 3, 4 and 5 from hydrogen pyrolysis show the effect of extensive hydrogenation through reaction (10) (ring hydrogenation). However, the hydrogen to carbon ratios do not reflect a large difference (see Figure 6). The explanation is that although reaction (10) adds hydrogen to the aromatic structure, net hydrogen is also lost from the molecule through reaction (8). Hydrogen pyrolysis liquids are more hydroaromatic, but with less side chains. The stripped side chains partially explain the formation of high methane yields during hydrogen pyrolysis.

CONCLUSIONS

The M-SESC technique used here, and accompanied by further characterization of each one of the fractions, is demonstrated as a powerful tool that allows a deep insight into coal pyrolysis liquids structure and composition.

Basic differences in the structure and composition of coal liquids, revealed through MBSESC and fraction characterization techniques has been explained in this work through the thermal reactions where hydrogen participates.

The characterization technique, and the discussion offered here, presents an extra dimension in the understanding of coal pyrolysis liquids and the reactions that form them and the reactions where they participate.

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TABLE 1

COMPOSITION OF WESTERN KENTUCKY NO. 9 COAL

(Weight Percent)

Carbon	74.17
Hydrogen	5.12
Nitrogen	1.19
Sulfur	2.64
Oxygen (by difference)	7.31
Ash (MF)	9.57
Volatile Matter	35.30

TABLE 2

AVERAGE PROPERTIES OF COAL LIQUIDS

(Before M-SESC Fractionation)

	Flash Hydrogenation	Steam/He Pyrolysis
Carbon	87.01	81.61
Hydrogen	5.60	4.60
Nitrogen	1.55	2.37
Oxygen + Sulfur	5.89	11.42
Hydrogen/Carbon Ratio	0.77	0.67
Number Ave. Molecular Size	172.00	209.00
% Aromatic Hydrogen (by NMR)	83.30	89.50

TABLE 3

STRUCTURE OF THE MODIFIED SESC FRACTIONS

FRACTION	STRUCTURE	BOILING RANGE	DENSITY	AVE. MOL. SIZE
I	Aromatics, low heteroatoms	50 - 400 C	1.11	190
II	Aromatics, alkyl-aromatics, low heteroatoms	300 - 500 C	1.18	190
III	Polar aromatics, with non-basic heteroatoms	300 - 600 C	0.996	250 - 400
IV	Alkyl-polar aromatics phenol and methoxy groups	*	n.a.	250 - 400
V	Basic heterocyclics and phenol groups	*	n.a	300 - 400
VI	Basic heterocyclics alkyl and phenol groups	*	0.987	250
VII	Polyphenols, non-condensed aromatics high heteroatoms	*	n.a.	300 - 420
VIII	Polyphenol, alkyl chains	*	1.194	350 - 450

*Did not elute from G.C. in boiling point simulating analysis

FIGURE 1
Product Distribution from Hydrogen
and Steam/He Pyrolysis

COMPONENTS

HYDROGEN RUN

STEAM/HELIUM
RUN

INERT GAS
RUN

CARBON OXIDES

LIGHT HC GASES

B T X

LIQUIDS

TOTAL CONVERSION

MASS PERCENT
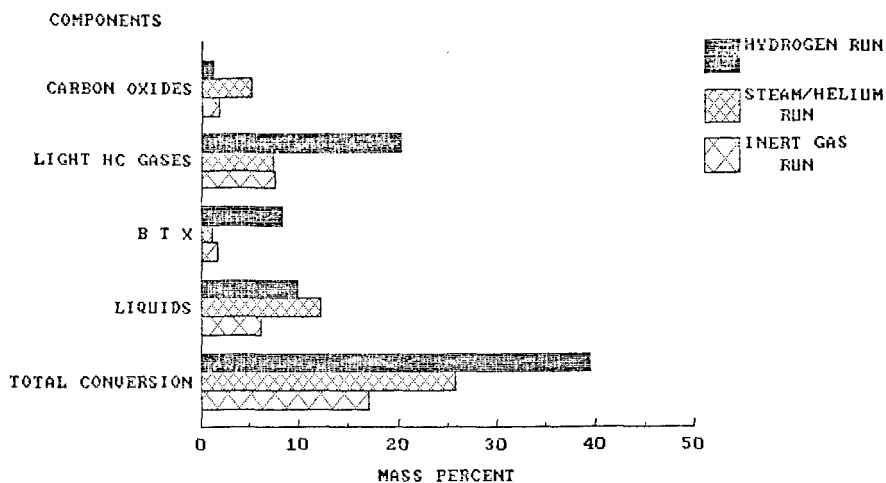
FIGURE 2 : M=SESC MASS DISTRIBUTION
OF FRACTIONS

MASS PERCENT

Hydrogen Pyrolysis
Liquids

Steam/He Pyrolysis
Liquids

FRACTION NUMBER
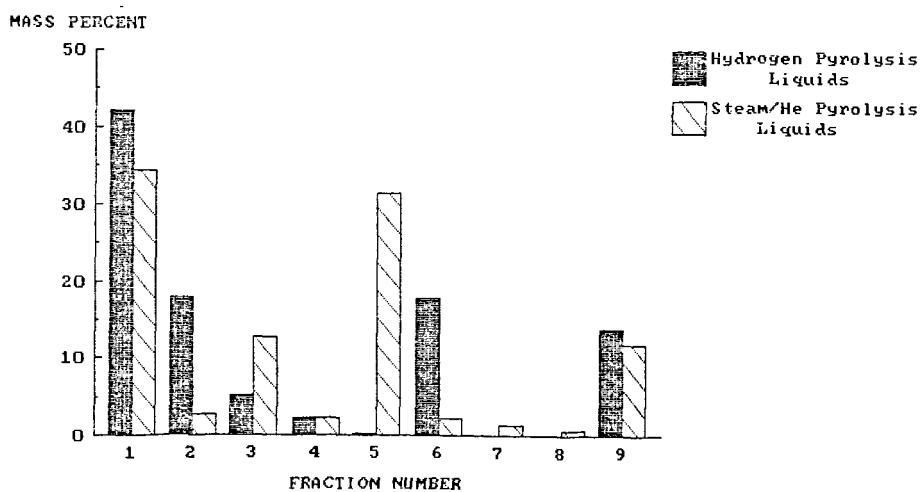
Fraction 9 is the mass not eluted.

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FIGURE 3 : AVERAGE MOLECULAR SIZES
OF M-SESC FRACTIONS.

MOLECULAR WEIGHT
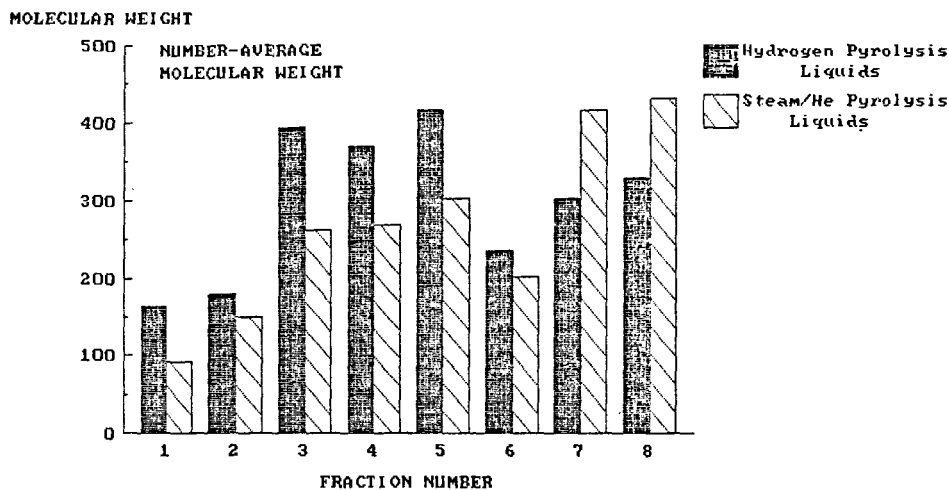
Obtained by Steric Exclusion HPLC

FIGURE 4
HYDROGEN AND NITROGEN CONTENT
OF M-SESC FRACTIONS

MASS PERCENT
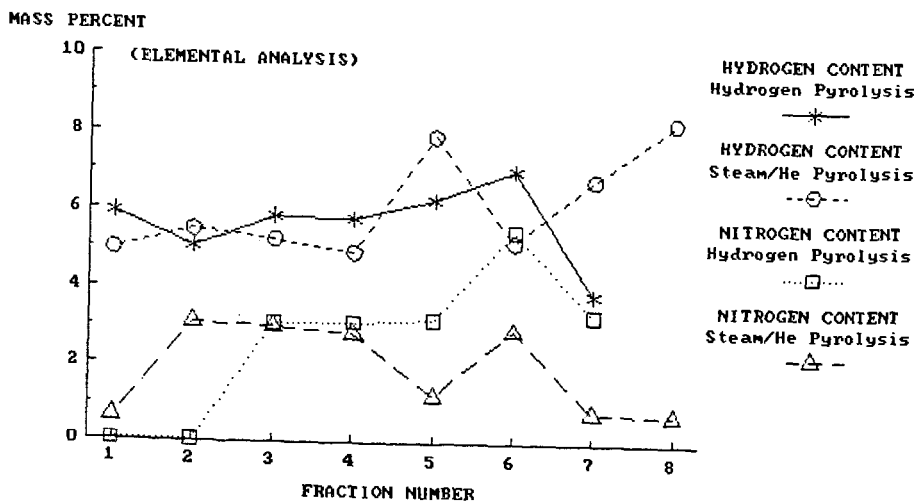
FIGURE 5
CARBON AND OXYGEN+SULFUR CONTENT
OF M-SESC FRACTIONS

MASS PERCENT

100 ┐ (ELEMENTAL ANALYSIS)

CARBON CONTENT
Hydrogen Pyrolysis
—✳—

CARBON CONTENT
Steam/He Pyrolysis
--⊙---

OXYGEN + SULFUR
Hydrogen Pyrolysis
····□····

OXYGEN + SULFUR
Steam/He Pyrolysis
—△—

FRACTION NUMBER
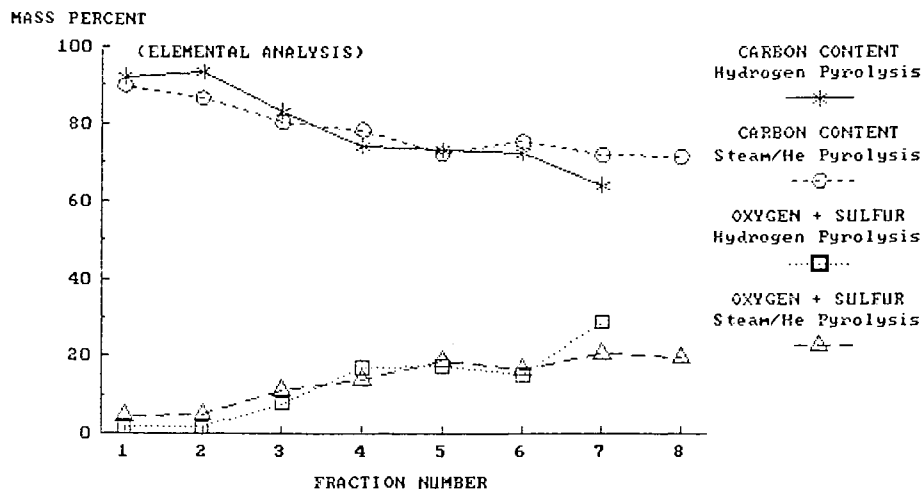
FIGURE 6
HYDROGEN TO CARBON RATIOS
OF M-SESC FRACTIONS

ATOMIC H/C RATIO

(ELEMENTAL ANALYSIS)

Hydrogen Pyrolysis
———

Steam/Helium
Pyrolysis
—△—

FRACTION NUMBER

381

FIGURE 7
AROMATICITY OF M-SESC FRACTIONS

% AROMATIC HYDROGEN

FIGURE 7
AROMATICITY OF M-SESC FRACTIONS
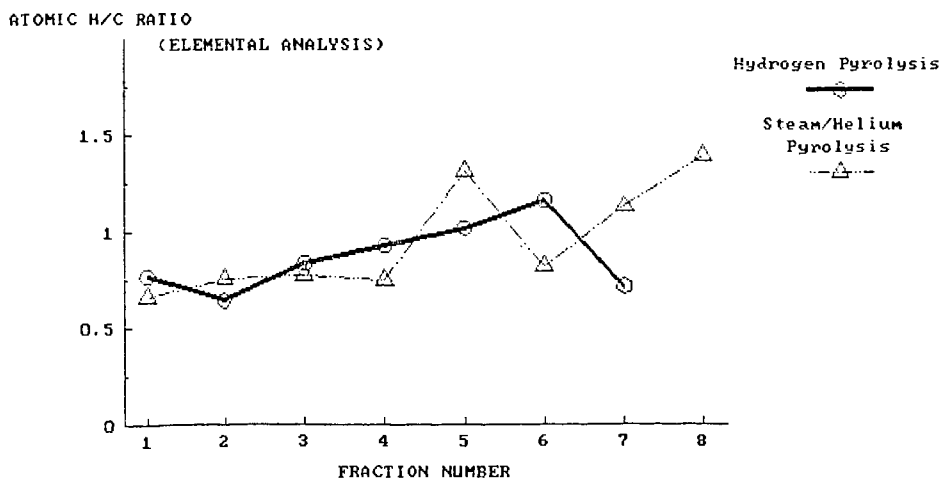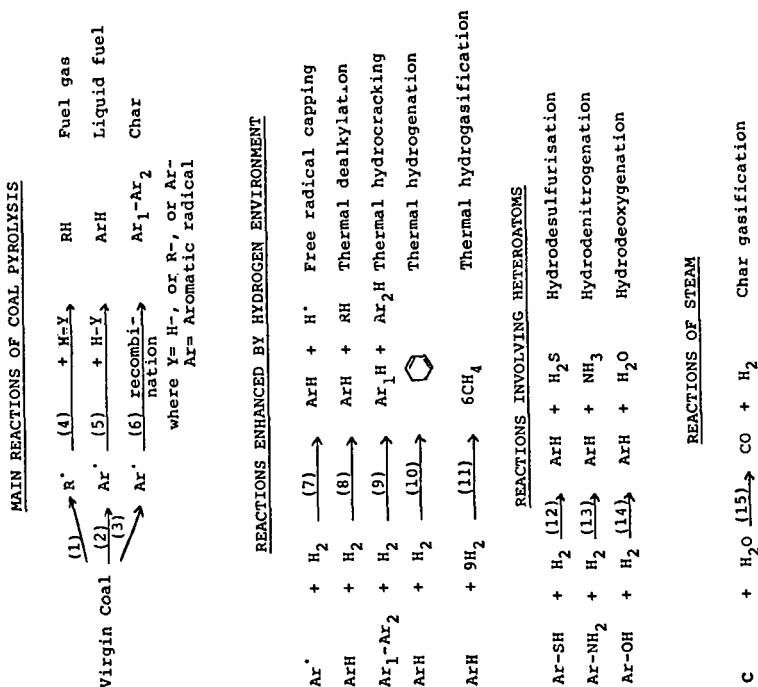
Figure 8   CHEMICAL REACTIONS IN STEAM AND HYDROGEN PYROLYSIS

MAIN REACTIONS OF COAL PYROLYSIS

$$Virgin\ Coal \xrightarrow{(1)} R^{\cdot}$$
$$\xrightarrow{(2)} Ar^{\cdot}$$
$$\xrightarrow{(3)} Ar^{\cdot}$$

$$R^{\cdot} \xrightarrow{(4)\ +M-Y} RH \quad Fuel\ gas$$
$$Ar^{\cdot} \xrightarrow{(5)\ +H-Y} ArH \quad Liquid\ fuel$$
$$Ar^{\cdot} \xrightarrow{(6)\ recombination} Ar_1-Ar_2 \quad Char$$

where Y= H-, or R-, or Ar-
Ar= Aromatic radical

REACTIONS ENHANCED BY HYDROGEN ENVIRONMENT

$$Ar^{\cdot} + H_2 \xrightarrow{(7)} ArH + H^{\cdot} \quad Free\ radical\ capping$$
$$ArH + H_2 \xrightarrow{(8)} ArH + RH \quad Thermal\ dealkylation$$
$$Ar_1-Ar_2 + H_2 \xrightarrow{(9)} Ar_1H + Ar_2H \quad Thermal\ hydrocracking$$
$$ArH + H_2 \xrightarrow{(10)} \hexagon \quad Thermal\ hydrogenation$$
$$ArH + 9H_2 \xrightarrow{(11)} 6CH_4 \quad Thermal\ hydrogasification$$

REACTIONS INVOLVING HETEROATOMS

$$Ar-SH + H_2 \xrightarrow{(12)} ArH + H_2S \quad Hydrodesulfurisation$$
$$Ar-NH_2 + H_2 \xrightarrow{(13)} ArH + NH_3 \quad Hydrodenitrogenation$$
$$Ar-OH + H_2 \xrightarrow{(14)} ArH + H_2O \quad Hydrodeoxygenation$$

REACTIONS OF STEAM

$$C + H_2O \xrightarrow{(15)} CO + H_2 \quad Char\ gasification$$

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